Heterometal Lanthanide Group 12 Metal Iodides

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Neodymium tri-iodide reacts with Group 12 metal (M; M = Zn, Cd, Hg) iodides to form heterometallic compounds. These Lewis acidic M cleave Nd–I bonds to give either ionic {[(THF)5NdI2][Ml3THF]; M = Zn, Cd} or charge-neutral {[(THF)5NdI2][Hg3]} compounds. Differences in structure are interpreted primarily in terms of M–L bond strengths, rather than Nd–L bond strengths. Experiments with Yb indicate that if there is any excess iodide present in these syntheses then the most readily isolated product is a triiodide salt, i.e., {[(THF)5YbI2][I3]}. In conventional solvents the presence of Lewis acid is not required for iodide displacement—from pyridine, “YbI3” crystallizes as {[(py)5YbI2][I3]}. These compounds are potentially useful as heterometallic sources of lanthanide-doped iodide matrixes, they illustrate the ease with which iodides are displaced from lanthanide coordination spheres, and they underscore the complexity associated with using lanthanide iodides as Lewis acid catalysts.

Introduction

Heterometallic compounds containing lanthanides (Ln) and transition metals (M) continue to be investigated as potentially useful electronic materials with readily tailored electronic or magnetic properties.1–7 This chemistry is compli-

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enough, simple homoleptic halides have never been used as starting materials in heterometallic syntheses. Such an uncomplicated approach to heterometallic chemistry could present an entry to new optoelectronic materials, as metal halide lattices have relatively low phonon energies, and so Ln-doped halide matrixes have potentially useful transmission windows.

In this work we outline our first attempts to prepare heterometallic iodide compounds containing both Ln and the group 12 metals Zn, Cd, and Hg. Difficulties associated with producing heterometallic iodides are identified, and the various structures of isolated heterometallic compounds are discussed in terms of relative M–I bond strengths.

**Experimental Section**

**General Methods.** All syntheses were carried out under high-purity nitrogen (Airgas), using conventional drybox or Schlenk techniques. Solvents (Aldrich) were either refluxed continuously over molten alkali metals or K/benzophenone and collected uncorrected.

**Synthesis of [(THF)$_3$NdI$_2$][(THF)ZnI$_3$] (2).** Nd (0.29 g, 2.0 mmol) and I$_2$ (0.76 g, 3.0 mmol) were combined in THF (25 mL). The mixture was stirred until most of the metal was consumed (2 days) to give a translucent pale brown solution. Zn (0.13 g, 2.0 mmol) and more I$_2$ (0.51 g, 2.0 mmol) were added to the mixture and stirred for 2 days. The solution was allowed to settle and a tan solid precipitated. The rust solution was filtered (30 mL) and layered for 2 days. The solution was allowed to settle and a tan solid formed. Zn (0.13 g, 2.0 mmol) and more I$_2$ (0.51 g, 2.0 mmol) were added to the mixture and stirred for 4 days. The mixture was allowed to settle and the tan precipitate was separated from the golden yellow solution by filtration. The solution (22 mL) was layered with hexanes (13 mL) to give colorless rods (0.56 g, 22%) that turn black at 140 °C and melt at 255 °C. Anal. Calcld for C$_{20}$H$_{40}$O$_5$NdHgI$_5$: C, 17.9; H, 3.01. Found: C, 17.5; H, 3.15. The compound is colorless, but exposure to air produces an optical absorption maximum at 368 nm in THF.

**Synthesis of [(THF)$_3$NdI$_2$][(THF)CdI$_3$] (3).** As for 2, Nd (0.29 g, 2.0 mmol), I$_2$ (0.76 g, 3.0 mmol), THF (25 mL), Cd (0.23 g, 2.0 mmol), and more I$_2$ (0.51 g, 2.0 mmol) gave colorless lathes (0.40 g, 19%) that turn black at 150 °C and melt at 255 °C. Anal. Calcld for C$_{20}$H$_{40}$O$_5$NdCdI$_5$: C, 21.8; H, 3.65. Found: C, 20.8; H, 3.86. The compound is colorless, but exposure to air produces an optical absorption maximum at 368 nm in THF.

**Synthesis of [(py)$_5$YbI$_2$][I$_3$] (5).** Yb (0.35 g, 2.0 mmol) and I$_2$ (0.72 g, 2.9 mmol) were combined in THF (40 mL). The mixture was stirred until all the metal was consumed (3 days) to give a transparent pale yellow solution and a salmon pink precipitate. The precipitate was isolated by filtration, dried under vacuum, and dissolved in pyridine (25 mL) to give a transparent blue solution. After a day the solution was filtered to remove trace black precipitate, and layered with hexanes (20 mL) to give yellow needles (1.10 g, 50%) that turn black and melt at 375 °C. Anal. Calcld for C$_{27}$H$_{27}$N$_5$YbI$_5$: C, 33.4; H, 2.80; N, 7.79. Found: C, 33.2; H, 3.05; N, 7.65. The compound does not show an optical absorption maximum from 300 to 800 nm in pyridine and was insoluble in THF.

**Synthesis of [(py)$_5$YbI$_2$][I$_3$]-1/2(py) (4).** Yb (0.35 g, 2.0 mmol) and I$_2$ (0.76 g, 3.0 mmol) were combined in THF (50 mL). The mixture was stirred for 3 days to give pink powder and a light yellow solution. The solution was filtered, concentrated to 38 mL, and was stirred for 3 days to give pink powder and a light yellow solution. The solution was filtered and layered with hexanes (25 mL) to give long yellow needles (0.59 g, 25%) that turned brown at 201 °C but did not melt below 296 °C. Anal. Calcld for C$_{20}$H$_{40}$O$_5$I$_5$: C, 22.6; H, 4.10. The compound is colorless, but exposure to air produces an optical absorption maximum from 300 to 800 nm in pyridine and was insoluble in THF.

**X-ray Structure Determination of 1, 2, 4, and 5.** Data for 1, 2, 4, and 5 were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K. The data were corrected for Lorenz effects and polarization, and absorption, the latter by a multiscan (SADABS) method. The structures were solved by Patterson or direct methods (SHELXS86). All non-hydrogen atoms were refined (SHELXL97) based upon $F_{o}^2$. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).

Scattering factors ($f$, $f'$, $f''$) are as described in SHELXL97. Crystallographic data and final R indices for 1, 2, 4, and 5 are given in Table 1. ORTEP diagrams for 1, 2, 4, and 5 are shown in Figures 1, 2, 3, and 4, respectively. Significant bond geometries for 1, 2, 4, and 5 are given in the figure captions. Complete crystallographic details for 1, 2, 4, and 5 are given in the Supporting Information.

(10) Bruker-ASX. SADABS, Bruker Nonius Area Detector Scaling and Absorption Correction, v2.05; Bruker-AXS Inc.: Madison, WI, 2003.


Table 1. Crystallographic Data and Final R Indices for 1, 2, 4, and 5

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$^a$ R(F) = $\sum|F_o| - |F_c|/|\sum F_o|; R_w(F)^2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$. Additional crystallographic details are given in the Supporting Information.

Results

The group 12 metal iodides MI$_2$ (M = Zn, Cd, Hg) react with LnI$_3$ to form heterometallic compounds with a transfer of iodide from Ln to M. Saturation of a THF solution of HgI$_5$NdI$_3$ results in the isolation of [THF]$_5$NdI$_2$[THF]CdI$_3$ (1).

A low-temperature single-crystal X-ray diffraction analysis of this product revealed a structure with pentagonal bipyramidal geometry about the Nd, having two axial I$^-\Gamma$ and five equatorial THF ligands. Figure 1 gives an ORTEP diagram of 1, with significant bond lengths and angles in the figure caption. In the structure of 1, all I$^-\Gamma$ has been extracted from the Nd(III) coordination sphere, and this I$^-\Gamma$ coordinates the Hg(II) ion. One of the Nd bond I$^-\Gamma$ also coordinates to the Hg(II) ion, and while there are four I$^-\Gamma$ about the Hg, the geometry is better described as trigonal planar HgI$_3$ with a relatively weak, e.g. dative, interaction between Hg and I(2).

The three terminal iodides on Hg have similar bonding geometries, both in terms of bond lengths [Hg(1)–I(4), 2.7146(6) Å; Hg(1)–I(5), 2.7206(6) Å; Hg(1)–I(3), 2.7250(5) Å] and angles [I(4)–Hg(1)–I(5), 122.05(2)$^\circ$; I(4)–Hg(1)–I(3), 119.78(2)$^\circ$; I(5)–Hg(1)–I(3), 114.43(2)$^\circ$]. In contrast, the distance between Nd and I(2) is 2.5424(3) Å, and the average I(2)–Hg–I angle is 96.5$^\circ$. The mutual effects of each metal on the others M–iodide bond length is apparent not only in the Hg–I bond but also, in a less dramatic way, in the bonds to Nd, where the Nd–I(1) bond length is 3.0543(6) Å and Nd–I(2) bond length is longer at 3.1086(6) Å.

The more acidic MI$_2$ compounds also extract I$^-\Gamma$ from LnI$_3$, but the bridging Ln–I$^-\Gamma$–M interaction present in 1 has been disrupted by THF coordinated to both Ln and M to give the ionic compounds [(THF)$_5$NdI$_2$][(THF)MI$_3$] (M = Zn(2), Cd(3)). Figure 2 gives an ORTEP diagram of 2, with significant bond lengths and angles in the figure caption. The unit cell data for the Cd compound 3 indicated that it is isostructural with 2. The cationic Nd fragment has considerable precedence in the literature, while the overall geometries of the main group anions are similar to those of other M(II) anions.
Similarly, when an excess of iodine is added to YbI₃ in THF the resultant deep red solution can be saturated to give \([\text{THF}_2\text{YbI}_2][\text{I}_3]\) (5), a salt that can be prepared in 25% yield. These yellow-orange crystals routinely grow to >1 cm long. Structural characterization of 5 revealed a cationic structure similar to that found in 4, with a pentagonal bipyramidal Yb(III) ion containing two axial I⁻ and five equatorial THF ligands. The counterion in this case was the well-known triiodide, \(\text{I}_3^-\). Figure 4 gives an ORTEP diagram of 5, with significant bond lengths and angles included in the figure caption. Tri-iodides were always noted as minor cocrystallized products in the synthesis of 1–4 if an excess of I₂ was present, or if solutions of these compounds were exposed to air.

Discussion

Of the three heterometallic products described herein, only the mercury compound 1 crystallizes as a molecular product, with the Zn and Cd analogues 2 and 3, as well as the pyridine complex 4 and triiodide compound 5, crystallizing as salts. All compounds serve to illustrate the particular ease with which iodides are removed from lanthanide coordination spheres. Variations in the Group 12 compounds reflect the relatively covalent nature of Hg, compared with Cd or Zn. Precedence for MI₃⁻ and MI₂²⁻ anions is noted for all three of the group 12 metals.

Iodide chemistry of the Group 12 metals has been thoroughly examined. Mercuric iodide is certainly the most complicated of the group. A light-sensitive material, solid-state HgI₂ is complex, with a remarkable range of Hg–I interactions: there is a red form containing Hg in a distorted tetrahedral geometry [four 2.783 Å Hg–I bonds, I–Hg–I = 103.1° and 112.7°], and a yellow form that contains essentially linear HgI₃ molecules (I–Hg–I = 178.3°) with two short (2.615 and 2.620 Å) and four long (2 × 3.507 Å and 2 × 3.510 Å) Hg–I bonds. HgI₂ has often incorporated additional I⁻ within the primary Hg(II) coordination sphere, resulting in a multitude of Hg coordination geometries. Compound 1, with three well-defined Hg–I bonds (bond lengths range from 2.7146(4) to 2.7250(5) Å and average 2.720(1) Å) can be described either as a grossly distorted tetrahedron or a trigonal planar Hg with an additional weak Hg–I (3.2452(3) Å) interaction. Precedence for each type of geometry already exists. It should be noted that in the absence of Lewis base solvents, there appears to be no reaction of HgI₂ with LnI₃.

Solvent selection is crucial to the isolation of heterometallic iodides. In pyridine, analogous reactions did not yield a crystalline product with Nd. However, saturation of solution containing YbI₃ in pyridine results in the crystallization of \([(\text{py})_5\text{YbI}_2][\text{I}_5]\) (4) an ionic compound with a pentagonal bipyramidal Yb ion having two axial iodides, five equatorial pyridine ligands, and the monoanion I⁻. Figure 3 gives an ORTEP drawing of the molecule, with significant bond lengths and angles given in the figure caption. Both Yb–I and Yb–N bond lengths are consistent with previously reported trivalent Yb compounds. The deep yellow color of this compound presumably originates from an iodide to ytterbium charge-transfer absorption that ttails from the UV into the visible spectrum.

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Introduction of Lewis bases leads to a rich HgI₃ coordination chemistry, with an even more complicated range of Hg coordination geometries. In addition to the plethora of regular and distorted T₄ structures, there are compounds such as R₅PPh₃HgI₃, a trigonal bipyramidal molecule with three strong bonds to Hg (P, I, I) and two weak HgI interactions between neighboring molecules. In this class of materials, structures often appear to be influenced by lattice requirements, brought to prominence because bonds to Hg are generally less than robust and form more open complexes with lower coordination numbers, particularly when the ligands are relatively electropositive.

In 2 and 3, the more acidic MI₃ (M = Zn, Cd) moieties coordinate an additional THF ligand rather than the terminal I bound to Nd. Similar reactivity has been noted in chloride systems, for example where LaCl₄ reacts with FeCl₃ in the presence of OPPH₃ to give [OPPH₃]₂La[Cl₂][FeCl₄]. In the preparation of [(THF)₃YbCl₃][(THF)₂W(O)Cl₄], or in Cu chemistry, i.e., [GdCl₃(OPPh₃)₃][CuCl₄]. In these cases, the stronger chloride ligands are removed from Ln(III) in the presence of highly charged (Fe(III), W(V), Cu(II)) Lewis acids. The Cd product 3 could, conceivably, find use as a Ln-doping source in the synthesis of cadmium halide glasses.

Iodide extraction has often been noted in lanthanide chemistry, and can be achieved by interaction with either acids or bases. While it was long known that the strongest Lewis bases would displace I⁻ to form ionic materials, the diversity of reagents that cleave Ln—I bonds, as revealed in the present study, is surprising. Early work examining the coordination chemistry of LnI documented the formation of conducting solutions with a variety of Lewis bases, including urea, dimethylacetamide, ethylenediamine, DMSO, DMF, and bipyrimidine. The number of displaced iodides paralleled the donor strength, i.e., DMSO formed a 1:3 electrolyte whereas bipyrimidine displaced only a single I⁻.

The shift away from synthetic methodologies using these strong donor solvents, toward preparative inorganic/organometallic chemistry involving less polar solvents (i.e., THF, DME, pyridine) will certainly benefit from analyses of simple coordination chemistry, particularly if lanthanide iodides are to be developed as catalysts. In the present work, it is clear that even a monodentate nitrogen-containing donor such as pyridine is sufficiently basic so as to displace I⁻ from Ln(III) coordination spheres. This reactivity does not necessarily apply to the larger, early lanthanides, given that in the chemically similar actinium series, UI₃, which has an ionic radius slightly larger than Nd, crystallizes from pyridine as molecular (py)₄UI₃.

Displacement of I⁻ by pyridine is important when examining the catalytic behavior of lanthanide iodides, because it suggests that even in the conventional monodentate solvents currently used in synthetic chemistry, both neutral and charged species are possible. For example, in the reported polymerization of butyl-4-vinylbenzoate with SmI₃, the presence of SmI₃ had a dramatic impact on molecular weight distribution. Clearly, the possibility that ([THF]₃SmI₃⁺, Sm(THF)₃⁺), or polynuclear species are the superior catalysts must be considered. Related examples of I⁻ extraction by a Lewis acid can be found in reports describing the self- ionization of LnI₃ to give LnI⁺₄/LnI⁻₁⁴b,c,d.

Extraction of I⁻ from YbI₃ by I₂, as evidenced by the structure of 5, again serves as a reminder that catalysis with lanthanide iodides can be complicated by an abundance of neutral and ionic species in solution. Surprisingly, this compound is isostructural with the analogous La derivative, making this formulation one of the rare instances in which all the lanthanides can form an isostructural series of compounds. In the La and Yb crystal structures, the I⁻—I⁻ anions have inversion symmetry requiring equivalent I⁻—I⁻. It has often been noted that a slight excess of Ln enhances the yield of I⁻—III, presumably because any adventitious oxygen/water does not result in the generation of excess I₂, which would otherwise react with LnI₃ to form particularly insoluble (THF)₅LnI₃(I⁻).

This iodide chemistry has frequent parallels with pseudohalide ligand systems. With respect to cyanide ligands, there exist structures with CN linking ionic/covalent combinations such as Sm/Ni or Yb/Fe. There is also a thiocyanate bridge linking La and Hg where, as expected, N coordinates to La and S coordinates to Hg. In recently described chalcogenolate reactivity group 12 M(EPH)₃ compounds were used to stabilize Ln(EPH) compounds. Selenolates were often extracted from Ln(II) by Hg(II) ions, while more acidic metals such as Zn(II) or Fe(III) were necessary to effect SePh extraction from Ln(III). Thiolates have been displaced from...
Ln coordination spheres, but only in the presence of multidentate Lewis bases.29

Conclusion

Discrete complexes comprised of LnI$_3$ with the group 12 metal iodides MI$_2$ can be prepared and isolated either as ionic or molecular products. A common feature to all three products, the extraction of I$^-$ by M from the Ln coordination sphere, is also noted in the extraction of I$^-$ by I$_2$ and the displacement of I$^-$ by pyridine. All of these compounds illustrate the facility with which iodide is removed from Ln coordination spheres.

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Supporting Information Available: X-ray crystallographic files in CIF format for the crystal structures of 1, 2, 4, and 5. This material is available free of charge via the Internet at http://pubs.acs.org.